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ENHANCING CORROSION RESISTANCE BY A HYDROPHOBIC SURFACE FEATURE FOR MAGNESIUM ALLOY AZ91D

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Abstract

A simple hydrothermal pretreatment was applied, prior to conventional conversion coating process, to produce a unique nano-scale surface. Subsequent growth of a compact and stable conversion coating reinforced the corrosion resistance of magnesium alloy AZ91D and significantly prolonged their limited lifetime. Finally, a highly hydrophobic surface was generated on top of the conversion coating, which effectively reduced the contact between corrosive medium, and metal surface, and the overall corrosion rate. The morphologies of the hydrothermal pretreated surface, conversion coating and hydrophobic layer were observed using scanning electron microscopy; the crystal structure and the composition was analyzed and determined using X-ray diffraction and energy dispersive X-ray spectroscopy. Corrosion performance was evaluated by the measurement of polarization behavior and salt spray testing. Such a surface coating system imparted considerable corrosion protection to the AZ91D substrate, and electrochemical polarization test results were presented to describe mechanistic aspects.

Introduction

Magnesium (Mg) and its alloys are promising lightweight materials (density of 1.7 g/cm^3, which is two thirds of aluminium, 2.7 g/cm^3, and one fifth of steel, ≈ 7.85 g/cm^3), for construction, electronics, automobile, and aircraft industries, having a high strength-to-weight ratio, good mechanical properties and excellent castability [1, 2]. Thus Mg alloys continue to receive significant research attention. Aluminium and steel are the commodity metals found in the transportation sector (*i.e.* cars, trucks, trains, buses and aircraft). In all such cases, energy can be conserved if weight can be reduced. For example, a 'rule of thumb' is that for each percentage of automotive weight reduction there is a corresponding percentage drop in fuel consumption (and hence, greenhouse gas emissions).

However, the use of Mg-based materials is still far behind that of the other light metals, such as aluminum and titanium, due to their vulnerability to corrode when exposed to most aqueous environments that are neutral or acidic (particularly those which contain halide ions). Mg is highly reactive and rapidly develops porous, poorly adhesive and inhomogeneous oxide/hydroxide/carbonate films [3, 4], upon atmospheric exposure [5, 6], which are incapable of providing satisfactory protection to the underlying metal against corrosion [7].

There are two primary methods that have been exploited extensively to minimize the corrosion rate for Mg alloys. One of these is modifying bulk Mg alloy composition, such as adding alloying element or reducing content of iron. Modifying bulk Mg alloy composition can reduce corrosion rate to some level by still not enough to meet the requirements for practical uses.

In the past decades, many efforts have been tuned to grow a compact barrier coating on surface to isolate the base material from the environment as an effective pathway to minimize corrosion rate of Mg alloys [1, 8]. One of the advantages is that only surface properties could be altered, in meantime; on the other hand, the mechanical properties of the bulk materials can be fully maintained. The surface could be offered numerous functions to fulfil diverse applications, in addition to corrosion resistance.

Several surface coating techniques, including electro-/electroless plating, conversion coating, anodizing, hybrid coatings, and vapor-phase processes, have been developed [1, 8]. Of those, chemical conversion coating treatment has attracted most interests due to some of the features including low-cost, and easiness to be implemented [9], which has been extensively adopted in industrial processes. The natively formed loose film on Mg-based substrates can be removed/converted into protective film by chemical conversion treatments. Since chemical reaction is the major driving force to grow film on surface, the bonding strength between coating and substrate will be much higher than others, such as physical vapor deposition. No use of electricity and expensive equipment facilitates the transition of the technology form lab to industrial production.

Chen and Birbilis have developed a number of metal phosphate conversion coatings to protect Mg and its alloys again corrosion [10-12]. A calcium hydrogen phosphate (brushite) was readily formed on surface of pure Mg in a coating bath containing dilute calcium phosphate solution (0.01 M) [10]. The brushite was transformed into more stable and insoluble hydroxyapatite via alkaline post-treatment, which reduced the high corrosion rate of Mg in two orders of magnitude. When applying calcium phosphate coatings on Mg alloy AZ91D, it was found by the same authors that hydroxyapatite was generated only in the baths with low concentration of PO_4^{3-} and Ca^{2+} ions [11]. The low solute concentration shortens the lifespan of the coating bath and is not cost-effective for commercialisation. They adopted manganese phosphate system and proposed that the coating features, such as surface morphology, thickness, crystallinity and corrosion protectiveness were highly related to the operational parameters, including pH and temperature [12]. Although these phosphate conversion coatings could protect Mg alloys from corrosion over some period of time, the aquatic droplets containing corrosive medium, i.e. NaCl, are clinging to these hydrophilic surfaces and try to break the barrier coating and initiate corrosion on the underlying metal. Thus, it would be a premium solution to convert the hydrophilic coating surfaces into hydrophilic to minimize the contact between NaCl droplets and coatings and endow superior corrosion resistance.

In this study, a series of simple and environmentally friendly metal (Ca, Mn and Sr) phosphate based conversion coatings were deposited on Mg alloy AZ91D. A highly hydrophobic surface condition was applied onto the conversion coatings to further improve their resistance to corrosion in aqueous medium. The coating morphology and corrosion performance were characterized by SEM-EDX, potentiodynamic polarisation examination and salt spray tests.

Experimental

Specimen preparation

Commercially Mg alloy AZ91D, from the magnesium alloy supplier HNKWE (Henan Province, China) was used in this study. The actual alloy chemical composition was determined with inductively coupled plasma - optical emission spectrometer (ICP-OES Spectrometer Services, Coburg, VIC, Australia) and reported in Table 1. A Toshiba 250 ton clamping force cold chamber high pressure die casting (HPDC) machine was used to cast test plates of 70 × 60 × 2 mm in size. Specimens were ground progressively down to 1200 grit finish and used as substrate material.

Table 1 Composition of the AM-lite materials (wt%).

Alloy	Al	Zn	Mn	Si	Fe	Cu	Ni
AZ91D	9.1	0.8	0.24	0.031	0.023	0.015	0.0005

Surface pre-treatment and coating process

Prior to pre-treatment, the specimens were ultrasonicated in acetone at room temperature for 15 min and then in absolute ethanol for 10 min and rinse with deionised water thereafter. An alkaline-hydrothermal pre-treatment was conducted to activate AZ91D surface for subsequent conversion coating formation. Subsequent coating process was carried out in three different solutions which contained 0.1 M Sr-phosphate, 0.1 M calcium phosphate, or 0.1 M manganese phosphate salts. pH of the coating solutions was adjusted to be acidic level using nitric acid (HNO_3). Finally, the conversion coated Mg alloy AZ91D specimens were exposed to an ethanol solution of 1H, 1H, 2H, 2H-Perfluorooctyltriethoxysilane (PFOTES) at room temperature for 45 min and subsequently heated at 80 °C for 15 min. Two rinses in distilled water were applied between each step to remove chemical contamination at the surface. All chemicals used in this work were analytical grade from Sigma-Aldrich Ltd. Digital temperature controllers were used to maintain the bath temperature. Following the coating step, samples were dried and kept in a desiccator for further characterisation.

Surface and corrosion analysis

Surface morphologies were observed using scanning electron microscopy (SEM, FEI Nova). Contact angle measurement of the liquid droplets was conducted on the hydrophobic surface of conversion coated AZ91D samples by the sessile drop technique at room temperature using a KSV Cam101 contact angle meter. A microliter syringe pump was attached to a small needle in an XYZ manipulator to enable a drop to be slowly increased and decreased in size. The shape of the drops was recorded by a digital camera and the contact angles were measured from the images. The drop size was set at 8 μl. At least five droplets of pure water were used for each sample to obtain a mean value. For electrochemical tests, a flat-cell (PAR) was used with an electrode area of 1 cm^2. The reference electrode used was a saturated calomel electrode (SCE), and the counter electrode was Ti-mesh. The electrolyte solution was 3.5 wt% sodium chloride (NaCl). A Biologic® VMP-3Z potentiostat was used to execute potentiodynamic polarisation at a sweep rate of 1 mV/s. The polarization curves were used to determine i_{corr} (via a Tafel-type fit) using EC-Lab software (v.10.6). As a general rule, data fittings were executed by selecting a portion of the curve that commenced > 50 mV from E_{corr}, and i_{corr} was subsequently estimated from the value where the fitting intercepted the potential value of the true E_{corr}. More generally, polarization testing was also able to visually reveal comparative information related to the kinetics of anodic and cathodic reactions. Salt spray tests were carried out in a dry corrosion test cabinet (DCTC 600, Angelantoni Industrie, Italy), where the ASTM B117 standard was adopted.

Results and discussion

Surface morphology and chemical composition

Alkaline-hydrothermal pre-treatment has altered the original smooth surface finish of AZ91D into a loose structure containing nano-sized MgO particles detected by XRD (data not shown). Such a surface condition was expected to have a higher aspect ratio and quicker dissolution rate of MgO into coating solution, and thus accelerate the growth rate of conversion coating.

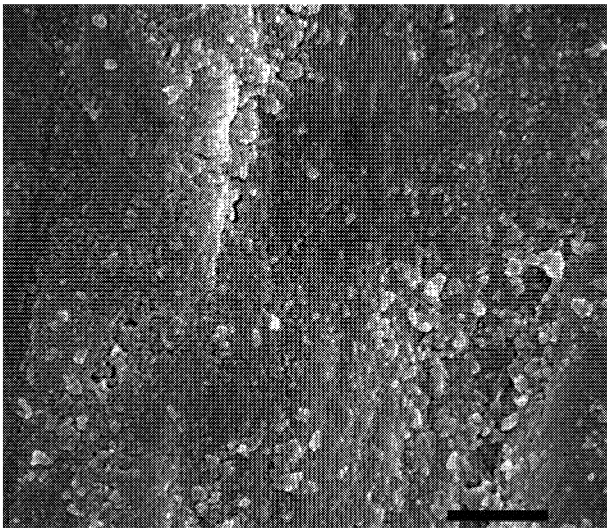
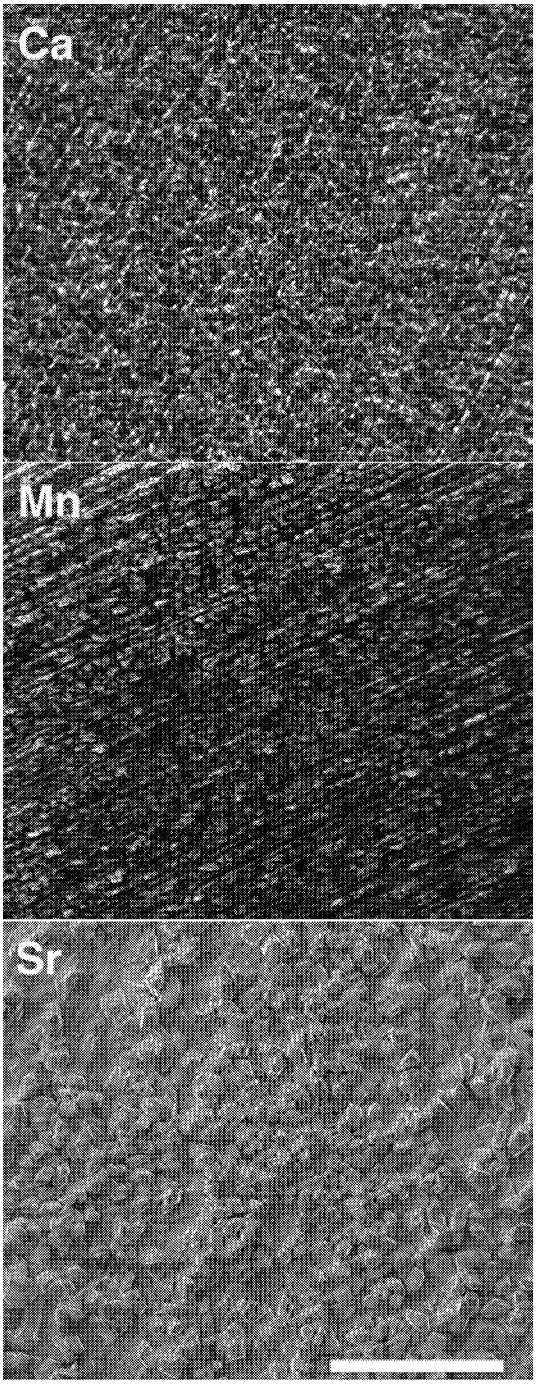


Figure 1. Surface morphology of alkaline-hydrothermal pre-treated Mg alloy AZ91D. Scale bar is 500 nm.

Surface morphology depicted in Figure 2 demonstrates that both Ca and Mn coatings are smooth and thin, since the contour of the grooves generated by the grinding process is still visible. But the presence of micro-cracks has been confirmed. Upon exposed to corrosive medium, chloride ions will easily approach to the substrate and trigger corrosion process through these defect sites. Thus, the existing cracks or defects would deteriorate the barrier effect and increase the corrosion rate eventually, though Ca and Mn phosphate coatings could tolerate the attacks from NaCl and maintain their role in protection at the initial period. In terms of Sr based conversion coatings, it can be seen that a uniform, compact and defect free coating with complete coverage was produced on Mg alloy AZ91D after 5 min immersion in the Sr-P coating bath. It is apparent that numerous cubic particles scattering on the top of the coating which reveals the high crystallinity of the deposits. In general, a coating with high crystallinity has a lower solubility in aqueous solution compared to amorphous phases. Consequently, such Sr-P based conversion coating is expected to be insoluble in NaCl solution and maintain its integrity for longer time, which is critical for long-term high corrosion resistance.



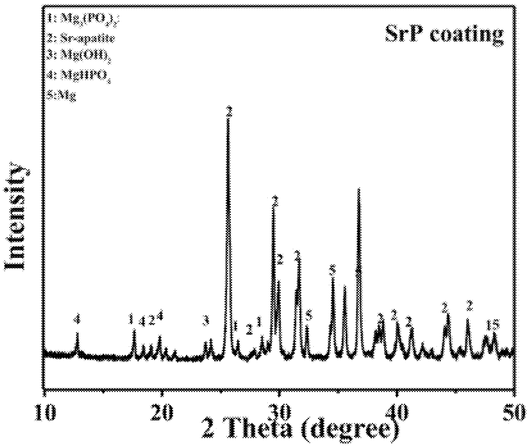


Figure 2. Surface morphology of Ca, Mn and Sr based conversion coatings and XRD spectrum of SrP coating on AZ91D. Scale bar is 100 μm.

Polarization curves and salt spray test

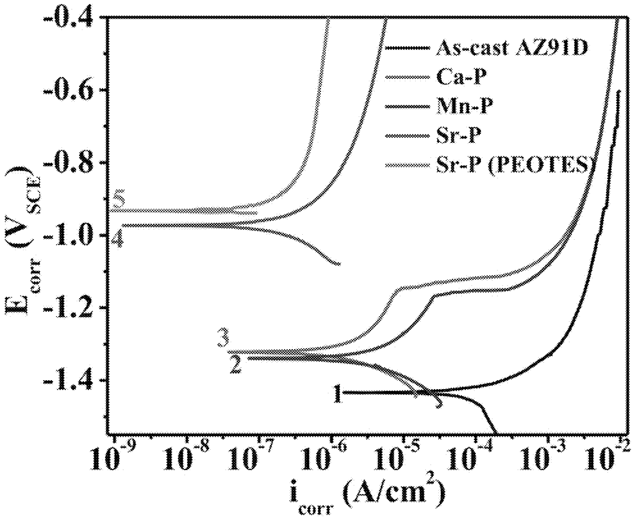


Figure 3. Polarization curves for various AZ91D in 3.5 wt% NaCl

In this study, corrosion rate of various coatings was examined via potentiodynamic polarization curves in 3.5 wt% NaCl and salt spray test according to the ASTM B117 standard. Polarization curves can be used to demonstrate instant anodic and cathodic reaction mechanisms as presented in Figure 3. The curve 1 (black line) for the as-cast Mg alloy AZ91D reveals the characteristic behavior of Mg alloy AZ91D metal whereby high corrosion rate are seen and the current (i_{corr}) rapidly increased with the application of anodic over-potential. Applying protective coating on AZ91D reduced the corrosion rate significantly by retarding both the anodic and cathodic reactions. Ca and Mn based conversion coatings drove the corrosion potential (E_{corr}) towards nobler region and the corrosion current moving towards left (curve 2 in red and curve 3 in blue). This is a clear sign for a protective feature offered by the barrier coatings. At least, at the initial immersion stage (before the breakdown potential point), the coatings isolated the substrates from attacks of corrosive medium, i.e. NaCl. Afterwards, the protection was gone and i_{corr} value increased sharply with the applied over-potential, similar to the case of as-cast AZ91D. In terms of Sr-coating (curve 4 in green), corrosion rate was profoundly decreased and E_{corr} was enhanced to nobler, compared to the Ca and Mn coated AZ91D cases, presenting a superior corrosion protective capability, which could be attributed to the dense, complete coverage and defect-free features of the Sr coating. It is worth mentioning the conversion coatings had a dominant impact in retarding anodic reactions (hence the coatings were a good resistor of ionic conduction) and a less (but some) influence on the cathodic reaction kinetics.

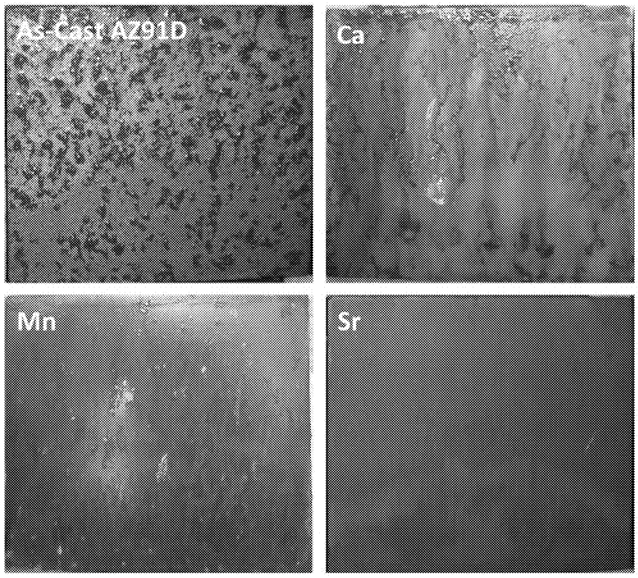


Figure 4. Various AZ91D specimens after 72 hours salt spray test.

Whilst potentiodynamic polarization measurement is a powerful tool to discover the dominant mechanisms behind the protection being afforded, the method is instantaneous in nature and hence supplementation with salt spray testing was executed. The corrosion performance of Sr coating was compared to uncoated AZ91D and CaP and MnP protective films using the salt-spray test. The salt spray test (according to the ASTM standard) involves continuously spraying 0.1M NaCl solution at 35°C from a nozzle into a chamber in which the samples are positioned. The corrosion performance was then assessed by visual inspection of the samples after being subjected to the salt spray. Obviously, over 85% surface area of the as-cast AZ91D sample corroded and was covered by white and grey corrosion product as presented in Figure 4. Though the corroded region fraction of AZ91D was minimized by the Ca-P and Mn-P based conversion coatings, corrosion still proceeded during the salt spray process, indicating that the supplied protection was limited and not satisfactory. With regards to the Sr coating, it can be seen that there was nearly no corrosion spots on the coated surface that still maintained its original integrity and features. Consequently, Sr coating had the best corrosion performance when compared to the other coatings, which is in agreement with the polarization results (Figure 3).

There are three key factors, i.e., the highest crystallinity, 100% surface coverage and defect-free morphology, which determine the high efficacy of SrP conversion coating in restriction of corrosion of Mg alloy AZ91D in NaCl electrolyte. A complete surface coating without noticeable defects can be an effective barrier to isolate underlying metal from the corrosive medium. Meanwhile, the high crystallinity endowed a low solubility and long-time stability to the SrP coating that degrades slowly when exposed to NaCl solution.

Since most corrosion media that the Mg alloys are exposed to, are aqueous solutions or moisture environment, a surface with water repelling functionality, i.e. hydrophobicity, is expected to be corrosion resistant. Thus, in this study, it was attempted to further enhance the corrosion resistance of the Sr-P conversion coating via tuning their original hydrophilicity into hydrophobicity. After post-treatment in PEOTES, the surface of the individual Sr-P based cubic particles has been covered with smaller precipitates (Figure 5), which contained element of F as detected by EDX. It was assumed to be a complex of PEOTES and Sr-P particles. Obviously, the corrosion potential of the hydrophobic Sr-P coating (contact angle above 120°) moved to nobler region and corrosion current density has been reduced, compared to the Sr-P coating (pink curve 5 in Figure 3). It is evident that hydrophobic functionality reinforced the protective role of the Sr-P coating against corrosion. But interestingly to note, the salt spray test did not display any significant difference in the corrosion protection of Sr-P and hydrophobic Sr-P coatings. That might be attributed to the low stability of the SrP-PEOTES complex.

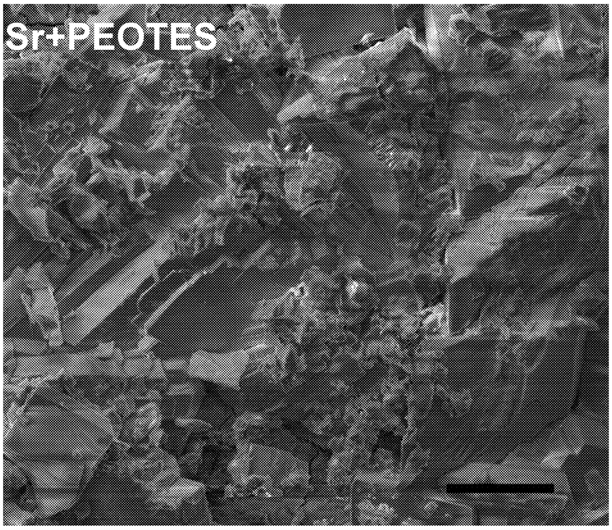


Figure 5. Hydrophobic SrP + PFOTES coating on Mg alloy AZ91D. Scale bar is 10 μm.

Conclusions

A simple conversion coating method, including pre- and post-treatment, was proposed and a series of Ca, Mn and Sr phosphate coatings were produced for corrosion protection of die cast Mg alloy AZ91D. The coating nature and corrosion performance were characterized by SEM-EDX, potentiodynamic polarization curves and salt spray test. Compared to the as-cast samples, all three coatings provided some protective function, more or less. Of these, the compact, complete and defect free Sr coating owned a superior corrosion resistance and its simplicity in operation will path a way for commercialization in the near future. The post hydrophobic treatment could further improve the corrosion resistance of the Sr-P coating during the initial stage though the long-term stability of the PEOTES-Sr complex compound is still a challenge.

Acknowledgements

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